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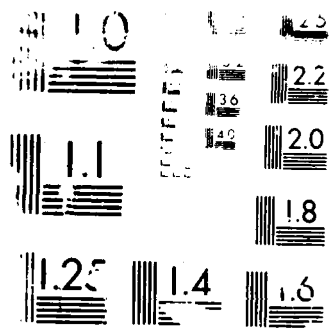

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FATIGUE CORROSION OF AMORPHOUS $Fe_{75-x}Cr_xB_{15}Si_{10}$ WIRES

BY LAWRENCE T. KABACOFF ANH H. LE

RESEARCH AND TECHNOLOGY DEPARTMENT

NOVEMBER 1986

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SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a REPORT SECURITY CLASSIFICATION UNCLASSIFIED	1b RESTRICTIVE MARKINGS
2a SECURITY CLASSIFICATION AUTHORITY	3 DISTRIBUTION AVAILABILITY OF REPORT Approved for public release; distribution is unlimited.
2b DECLASSIFICATION DOWNGRADING SCHEDULE	
4 PERFORMING ORGANIZATION REPORT NUMBER(S) NSWC TR 86-218	5 MONITORING ORGANIZATION REPORT NUMBER(S)
6a NAME OF PERFORMING ORGANIZATION Naval Surface Weapons Center — 6b OFFICE SYMBOL (If applicable) Code R32	7a NAME OF MONITORING ORGANIZATION
6c ADDRESS (City, State, and ZIP Code) 10901 New Hampshire Avenue Silver Spring, MD 20903-5000	7b ADDRESS (City, State, and ZIP Code)
8a NAME OF FUNDING SPONSORING ORGANIZATION — 8b OFFICE SYMBOL (If applicable)	9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
8c ADDRESS (City, State, and ZIP Code)	10 SOURCE OF FUNDING NUMBERS PROGRAM ELEMENT NO 62234N; PROJECT NO; TASK NO RS3455; WORK UNIT ACCESSION NO

11 TITLE (Include Security Classification)

Fatigue Corrosion of Amorphous $Fe_{75-X}Cr_XB_{15}Si_{10}$ Wires

12 PERSONAL AUTHOR(S)

Kabacoff, Lawrence T. and Le, Anh

13a TYPE OF REPORT	13b TIME COVERED	14 DATE OF REPORT (Year, Month, Day)	15 PAGE COUNT
	FROM ______ TO ______	1986 November	22

16 SUPPLEMENTARY NOTATION

17 COSATI CODES			18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	Amorphous Alloys, Iron, Silicon, Corrosion, Chromium, Fatigue Limit, Boron
07	02		
11	06	01	

19 ABSTRACT (Continue on reverse if necessary and identify by block number)

We have measured the fatigue and corrosion properties of metallic glass wires with the composition $Fe_{75-X}Cr_XB_{15}Si_{10}$ (X = 5, 8, and 10). Measurements were made in air, water, 3.5 w/o NaCl, and 1 N H_2SO_4. The observed fatigue limits are inversely proportional to the corrosion rate indicating a corrosion fatigue failure mechanism. Fatigue characteristics of the wires are vastly superior to melt spun metallic glass ribbons of similar composition, and superior to 304 stainless steel. Yield strengths up to 900 KSI have been observed (for 11 a/o Cr). Under certain circumstances, the wires are "self healing" in that if the cyclical strain applied to test specimens is interrupted prior to failure and then reapplied, the wire behaves in a manner identical to a new, unfatigued specimen. The corrosion characteristics of the wires are similar to those of melt spun ribbons of similar composition. Pitting and crevice corrosion in chloride environment are very slight or absent.

20 DISTRIBUTION AVAILABILITY OF ABSTRACT ☐ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT ☐ DTIC USERS	21 ABSTRACT SECURITY CLASSIFICATION UNCLASSIFIED
22a NAME OF RESPONSIBLE INDIVIDUAL Lawrence T. Kabacoff	22b TELEPHONE (Include Area Code) (202) 394-2645 — 22c OFFICE SYMBOL R32

DD FORM 1473, 84 MAR — 83 APR edition may be used until exhausted. All other editions are obsolete.

SECURITY CLASSIFICATION OF THIS PAGE

0102-LF-014-6602

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FOREWORD

This report describes the research performed during FY86 at the Naval Surface Weapons Center on high strength, corrosion resistant metallic glass wires. These wires, which have only recently become available due to the development of a new manufacturing process, hold considerable promise as a replacement for steel and titanium in many applications such as tow cables, mooring cables, and sonar domes. This work should be of interest to scientists and engineers who require very high-strength, ductile fibers which can tolerate a chloride environment with little or no corrosion (including pitting and crevice corrosion). This work was supported by NSWC's Independent Exploratory Development Program (IED-105) and by I. Caplen of the David Taylor Naval Ship Research and Development Center, Materials Ship and Submarine Block Program. Questions may be referred to Dr. Lawrence T. Kabacoff [(202)394-2645].

Approved by:

Jack R. Dixon

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Materials Division

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INTRODUCTION

Metallic glasses are non-crystalline alloys which are produced by rapid solidification either from the liquid or vapor phase.[1] Typical quench rates range between 10^5 and 10^9 C/sec. There are a large number of classes of metallic glasses. This report deals only with corrosion resistant Fe-based metallic glasses produced by quenching from the melt. These amorphous alloys typically contain about 25 a/o metalloid (usually B, Si, C, and/or P), with the balance comprised of various transition metals (Fe, Ni, Cr, and Mo). Because of the similarity in composition between these materials and 300 series stainless steels, they will be referred to as "amorphous stainless steels."

The corrosion resistance of amorphous stainless steels results from two effects.[2] Since the materials are truly non-crystalline and, therefore, lack grain boundaries and other crystalline defects, they form very high quality homogeneous passive films which especially resist pitting corrosion. Also, since the surface of an unpassivated metallic glass is in a higher energy state than a corresponding crystalline material, greater surface dissolution occurs prior to formation of the passive film. Thus, more beneficial ions (such as Cr) are present during passivation resulting in an enriched passive film. For example, a metallic glass with 10 a/o Cr may have a passive film with more than 50 a/o Cr. Passive films were 98 a/o of the metallic species is Cr have been observed. Such alloys can be boiled in 12 N HCl with no measurable corrosion.

Traditionally, amorphous stainless steels have been produced in the form of continuous thin ribbons by continuous chill block casting onto a copper wheel. These ribbons have very high yield strength (300-625 KSI) and excellent ductility in sheer. Tensile failure occurs in very narrow sheer bands.[3] Thus, the stress-strain curves resemble brittle materials even though the fracture surfaces show that this is not the case. The fatigue properties of ribbons are very poor, largely because the ribbons contian surface irregularities and large local variations in ribbon thickness. Generally, metallic glasses do not work harden. Because of the problems with fatigue, interest in using these materials for structural applications such as cables failed to develop.

A recent advance in fabrication technology has changed the situation. Unitika, Ltd of Japan has developed a process by which a stream of melt is injected directly into a moving layer of a water solution.[4] The entry angle and the relative speeds of the melt and water are adjusted to give a smooth, non-turbulent flow, resulting in high quality wires with round cross sections. Unitika engineers reported that the fatigue properties of the wires, unlike those of ribbons, are outstanding, and exceed those of, for example, 304 stanless steel.[5] These tests were carried out in air and deionized water. In all other respects, the properties of the wires were similar to those of ribbons with similar compositions. This development is extremely important to the Navy because of the strong need for high strength, corrosion resistant materials with outstanding fatigue properties for cable applications. However, before this technology can be exploited, several questions must be answered. First, the data presented by Unitika must be verified and extended to a seawater environment. This involves developing new compositions which represent the best compromise between the needs of corrosion resistance, strength, fatigue properties, and ease of fabrication into amorphous wires. Secondly, these wires must be tested under the extreme conditions experienced by the various tow and mooring cables used by the Navy. Finally, there must be a reasonable prospect that amorphous wire will be commercially available at a reasonable price.

These questions are being addressed by the current program, which consists of three phases: (1) developing compositions suitable for fabricating and testing; (2) developing reliable sources of test samples, including an in-house capability for producing research quantities of amorphous wires; and (3) determining the prospects for the availability of amorphous wires on a commerical basis. This report summarizes progress for FY86.

AVAILABILITY AND POTENTIAL COST OF METALLIC GLASS WIRE

At present, the only form of commercially available metallic glass is the continuous thin ribbon formed by continuous chill block casting. Typical dimensions are up to 7" wide by 0.0001" thick. The main applications are braising foils (Ni based alloys) and power distribution transformer cores (Fe based). The cost of the Fe based alloys is currently less than $2.00/lb and is expected to go much lower due to the competition of Si steels. The compositions currently being marketed are not suitable for chloride environments. Special compositions can be produced, but the low price would only be available to a high volume customer (e.g., ordering 1000 lbs or more).

Currently, the round cross section wires are produced commercially only by Unitika, Ltd of Japan, and production is limited to a pilot plant. Wire is available to American customers in amounts up to twenty pounds and only in three compositions. Research quantities (10 grams) of other compositions can be obtained, thus far at no cost. Unitika participates in an international venture company, NAMCO, whose two major partners are the Matsui Group and Allied Corp. Under this arrangement, Allied has given Unitika a license to manufacture the wires (Allied holds key patents) in exchange for exclusive distribution rights outside Asia.

At a recent meeting at the Naval Surface Weapons Center (NSWC), representatives of Unitika and Allied discussed the supply situation with engineers from NSWC and the David Taylor Naval Ship Research and Development Center (DTNSRDC). It was disclosed that the new pilot plant is producing about 100 kg per month at $60/lb. A production facility which could produce several tons per month is being considered. It was estimated that potential Navy consumption could exceed 100,000 lbs per year. The manufacturing situation changed very quickly because of recent interest in using metallic glass wires in tire cord. If successful, perhaps this will drive the cost of standard composition wire below $1.00/lb. Therefore, a plentiful, inexpensive supply of amorphous wire is very likely. Note that the compositions produced for the tire market will not be suitable for a chloride environment. However, the price of these wires is controlled almost entirely by the cost of building manufacturing facilities. The cost of raw materials and plant operation is somewhat less than those for producing conventional drawn wires. If start up costs are paid by the tire industry, the cost of "special order compositions," if orders are large enough, will be quite reasonable.

In the short term, small quantities of metallic glass wire (e.g., 10 grams) are sufficient to carry out corrosion, fatigue, and mechanical testing of monofilaments as a function of wire composition. Thus far, samples have been provided free of cost by Unitika. However, because of the delays involved and the numbers of compositions which will be needed, an in-house source is necessary. The parts for such an instrument have been obtained and are currently being assembled. It is expected that the facility will be operational soon. Quantities of wire suitable for fabrication of cables and tire cord can now be purchased from Unitika. They also have the expertise and are willing to fabricate the wires into a finished product.

EXPERIMENT

Following a review of the literature, the compositions $Fe_{75-x}Cr_xB_{15}Si_{10}$ (x = 5, 8, and 11) were selected for initial testing. This selection was based on the fact that, in the Fe-B-Si system, $Fe_{75}B_{15}Si_{10}$ has the maximum glass forming ability and a relatively high yield strength. The addition of Cr was expected to increase the strength while only moderately reducing the glass forming ability (as measured by the maximum diameter wire that can be made with no measurable crystallinity). The Cr, of course, is necessary for corrosion resistance. Carbon and phosphorus were not used as metalloids at this time because, while they enhance corrosion resistance (especially P), they reduce yield strength. Another important consideration was that these compositions had been produced previously by Unitika, and it was certain that samples could be obtained.

The apparatus for performing bending fatigue testing is illustrated in Figure 1. This device, which is similar to that used by Hagiwara et al.,[5] produces strain by passing a wire specimen over a pulley which is immersed in the medium of interest. The maximum strain is controlled by the diameter of the pulley and determined by the relation:

$$\epsilon = d/(d + D)$$

where d is the diameter of the wire (in this case .005") and D is the diameter of the pulley. Wire specimens were epoxyed to two nylon leads, one of which was tied to a wheel rotating at 2.0 Hz and the other weighted with a 100 gram load. Failure of the wire caused the weight to activate a switch connected to a timer. The number of cycles to failure was measured as a function of maximum strain. The fatigue limit was defined as the largest cyclical strain which would not result in failure within 10^6 cycles. Fatigue measurements were performed in air (65% RH), deionized water, 3.5% NaCl solution, and 1 N H_2SO_4.

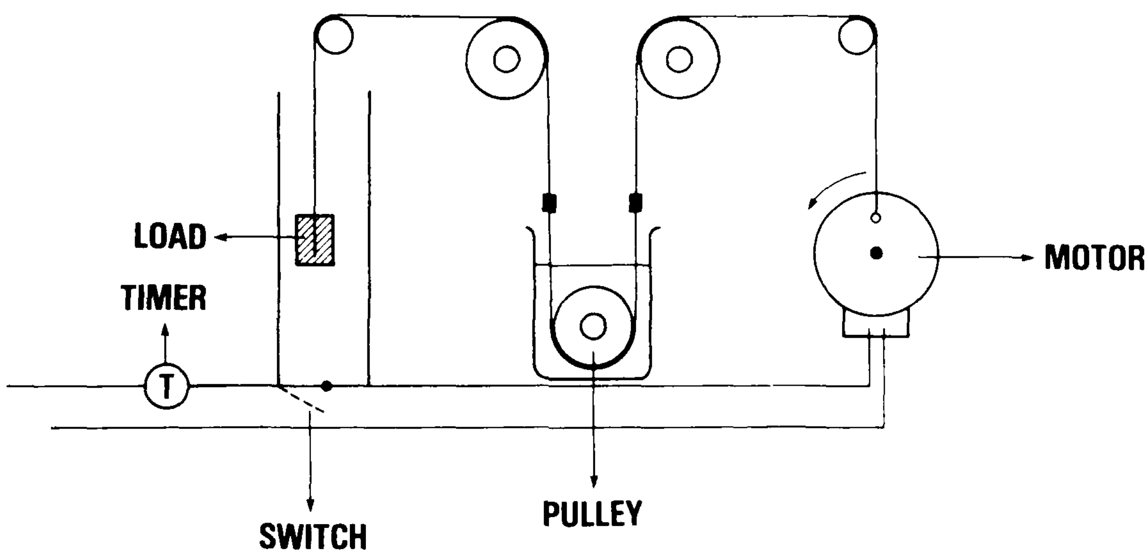

FIGURE 1. SCHEMATIC DIAGRAM OF THE APPARATUS USED TO MEASURE FATIGUE DUE TO CYCLICAL BENDING STRAIN

Potentiodynamic and pitting scans were obtained using an EG&G Corrosion Measurement Console (Model 350A). The three-electrode-cell consisted of a working electrode, a graphite counter electrode, and a SCE (saturated calomel electrode) reference electrode. Solutions of 3.5 w/o NaCl and 1.0 N H_2SO_4 were prepared from analytical grade chemicals and deionized water. Measurements were made at room temperature in aerated solutions. The initial potential for potentiodynamic curves was set at 250 mV below the open circuit potential. The scan rate was 1 mV/sec.

Finally, an approximate value for the tensile strength was obtained for each composition by hanging weights from the looped end of each wire. Several trials were made for each composition and the results averaged. The intention was only to get a rough estimate of the strength.

RESULTS AND DISCUSSION

Figure 2 shows polarization curves for amorphous wires in 3.5 w/o NaCl solution. The wires containing 5 a/o Cr display an active/passive behavior, while the 8 and 11 a/o Cr specimens exhibit complete passivity. As expected, the corrosion current density (and, therefore, the corrosion rate) decreases with increasing Cr content. All three compositions exhibited active/passive behavior in 1.0 N H_2SO_4 (Figure 3). As expected, the corrosion current decreased with increasing a/o Cr.

Pitting potentials varied only slightly as a function of composition in the NaCl solution (1.20 V/SCE for 5 and 8 a/o Cr, and 1.170 V/SCE for 11 a/o Cr). This is illustrated in Figures 4, 5, and 6 which show pitting scans for 5, 8, and 11 a/o Cr in 3.5 w/o NaCl, respectively. It is also apparent from these figures that the hysteresis is extremely small, indicating a very low rate of crevice corrosion. In 1.0 N H_2SO_4, all of the pitting potentials were the same (0.966 V/SCE).

Figures 7, 8, and 9 illustrate the number of cycles to failure as a function of maximum bending strain for 5, 8, and 11 a/o Cr, respectively. Fatigue limits were observed for each composition in air and deionized water, and for 8 and 11 a/o Cr in 3.5 w/o NaCl. Our data on moist air and deionized water agree well with published data by Hagiwara et al.[6] Comparison of Figures 2 and 3 with Figures 7, 8, and 9 clearly show the relationship between corrosion rate and fatigue limit (or number of cycles to failure), and that failure occurs through a corrosion fatigue mechanism.

In order to investigate the role of hydrogen in the corrosion fatigue failure of these alloys, wire specimens were immersed in 3.5 w/o NaCl, and subjected to cyclical bending strain for 15 minutes, then baked for 15 minutes. Without interruption, for the strain chosen, failure would occur after 40 minutes. This was repeated (15 minutes on, 15 off) for 8 hours without failure (a total of 4 hours of strain application).[8] This is consistent with the hypothesis that failure is due to accumulation of hydrogen. What was surprising was that the control specimens, which were not baked but were kept in the chloride solution during the "rest" period, also experienced no fatigue failures. In both cases, after the 8 hours of testing,

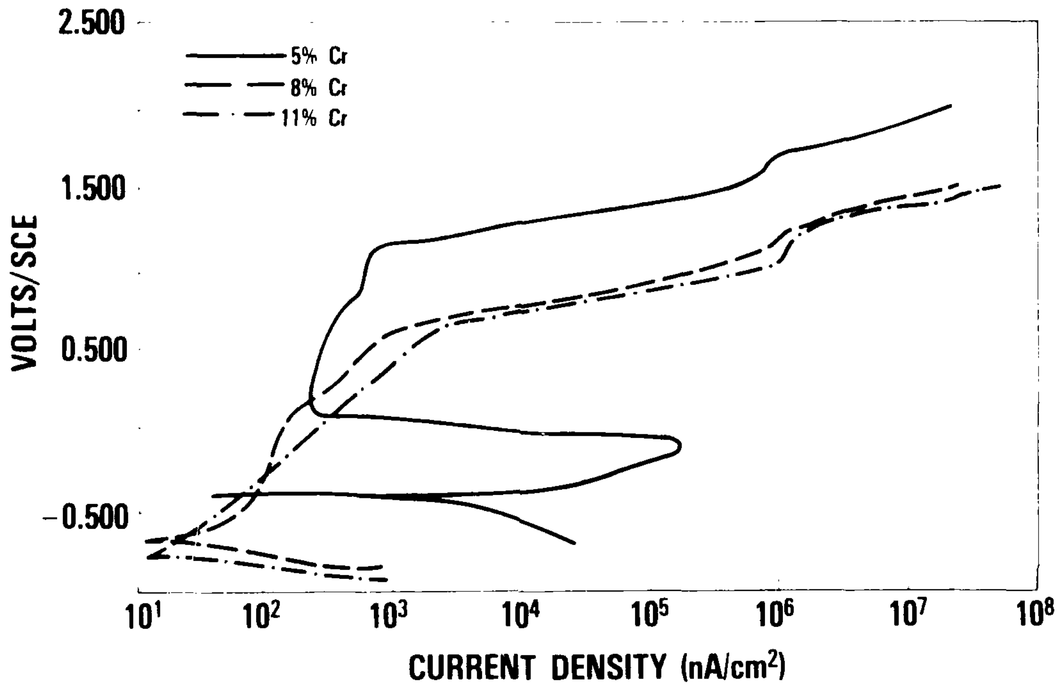

FIGURE 2. POTENTIODYNAMIC CURVES OF AMORPHOUS $Fe_{75-X}Cr_XB_{15}Si_{10}$ IN 3.5% NaCl

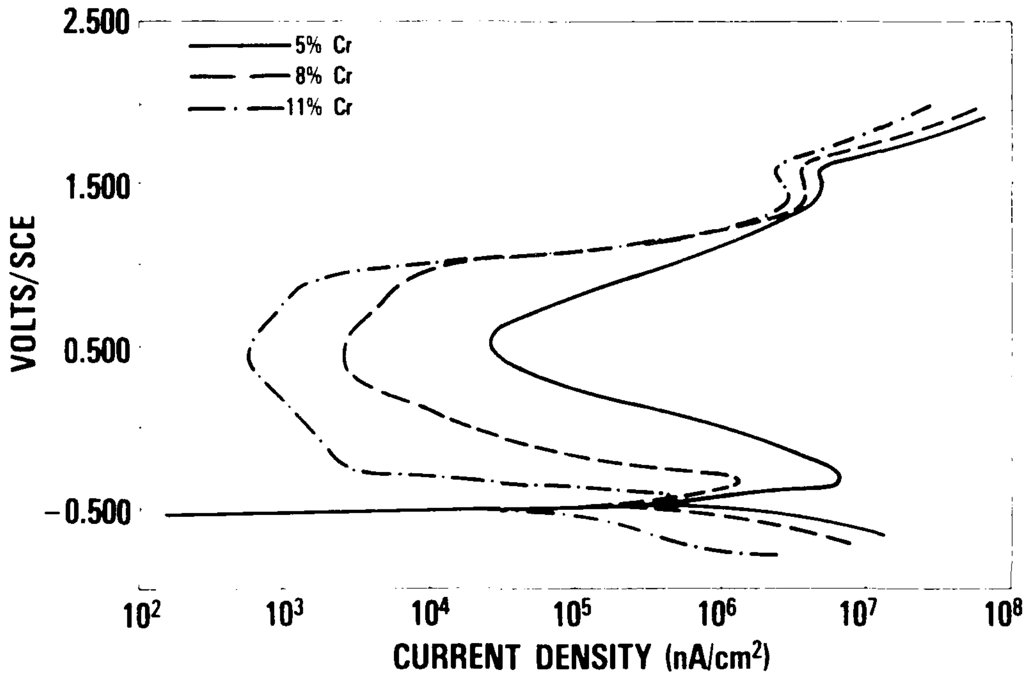

FIGURE 3. POTENTIODYNAMIC CURVES OF AMORPHOUS $Fe_{75-X}Cr_XB_{15}Si_{10}$ IN 1.0 N H_2SO_4

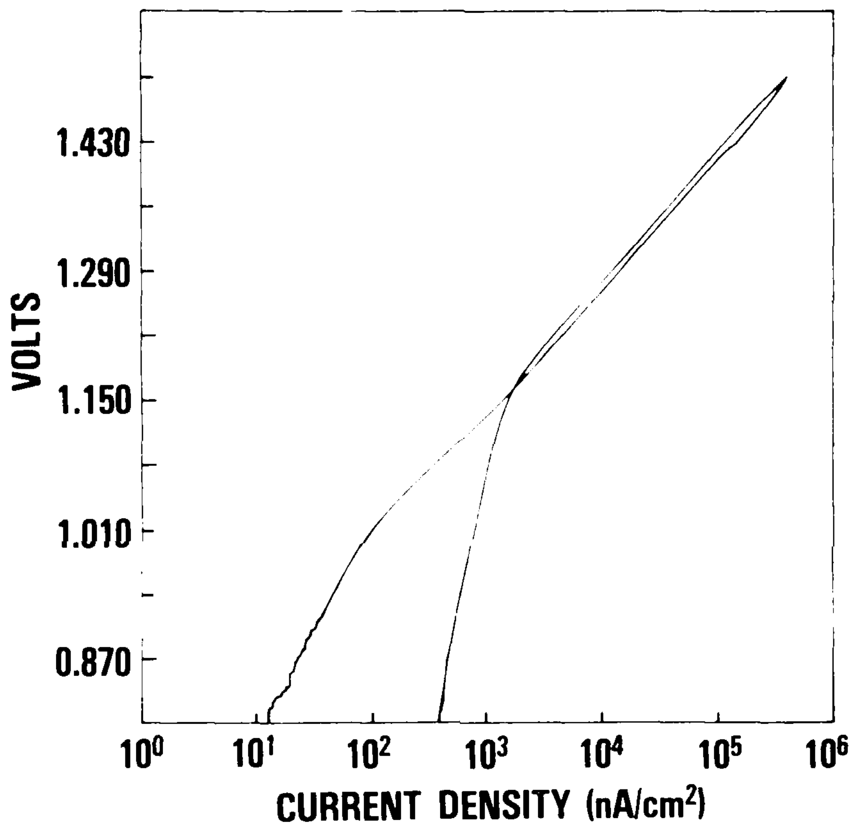

FIGURE 4. PITTING SCAN OF AMORPHOUS $Fe_{70}Cr_5B_{15}Si_{10}$ IN 3.5% NaCl

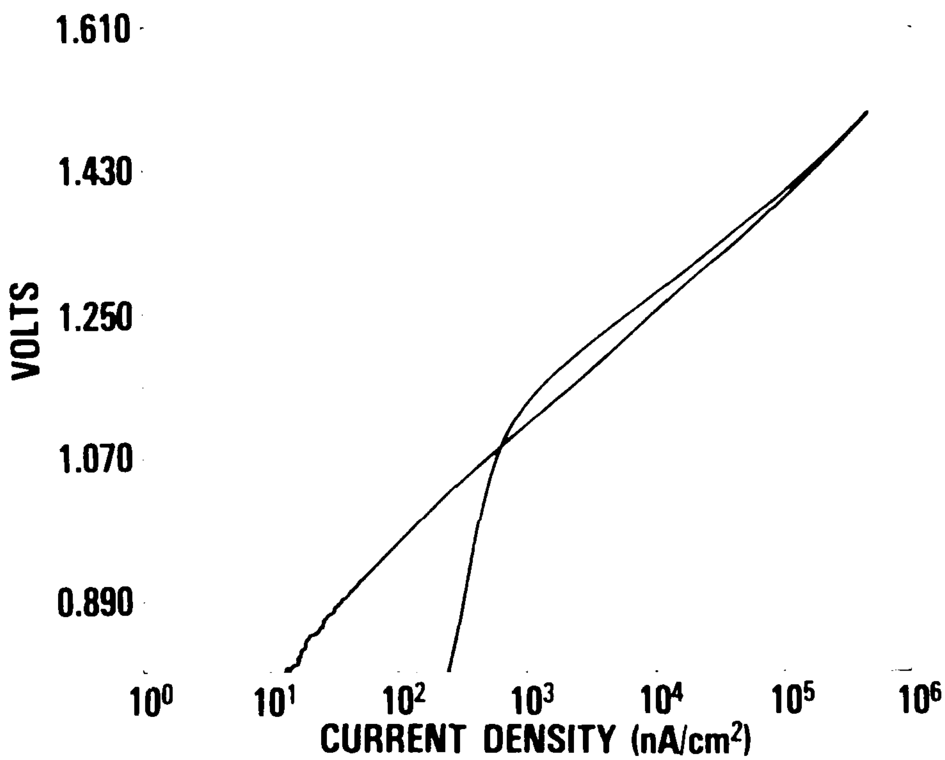

FIGURE 5. PITTING SCAN OF AMORPHOUS $Fe_{67}Cr_8B_{15}Si_{10}$ IN 3.5% NaCl

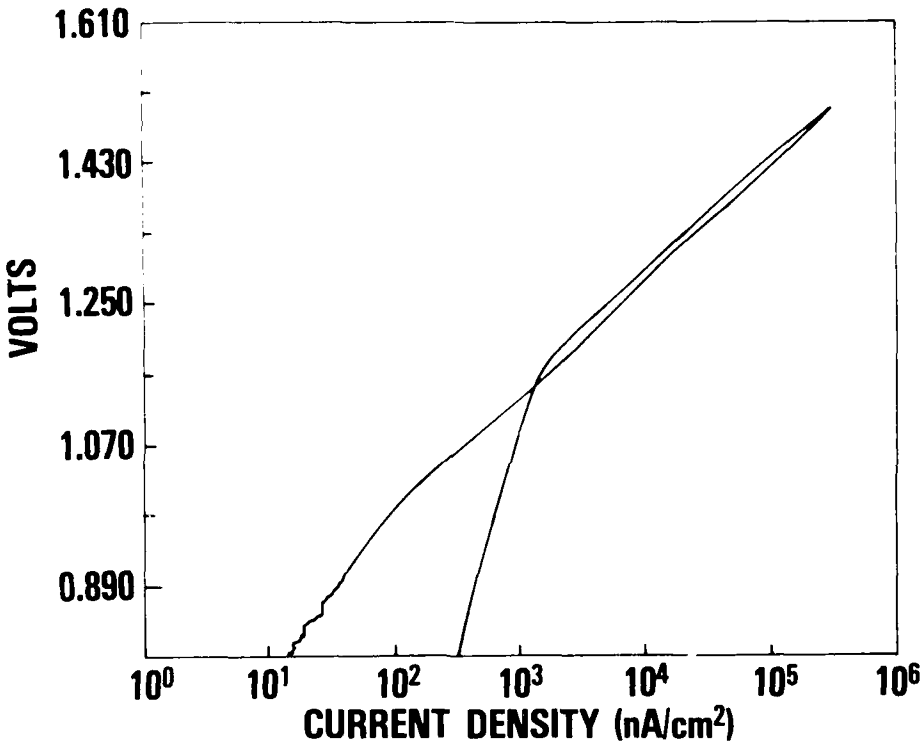

FIGURE 6. PITTING SCAN OF AMORPHOUS $Fe_{64}Cr_{11}B_{15}Si_{10}$ IN 3.5% NaCl

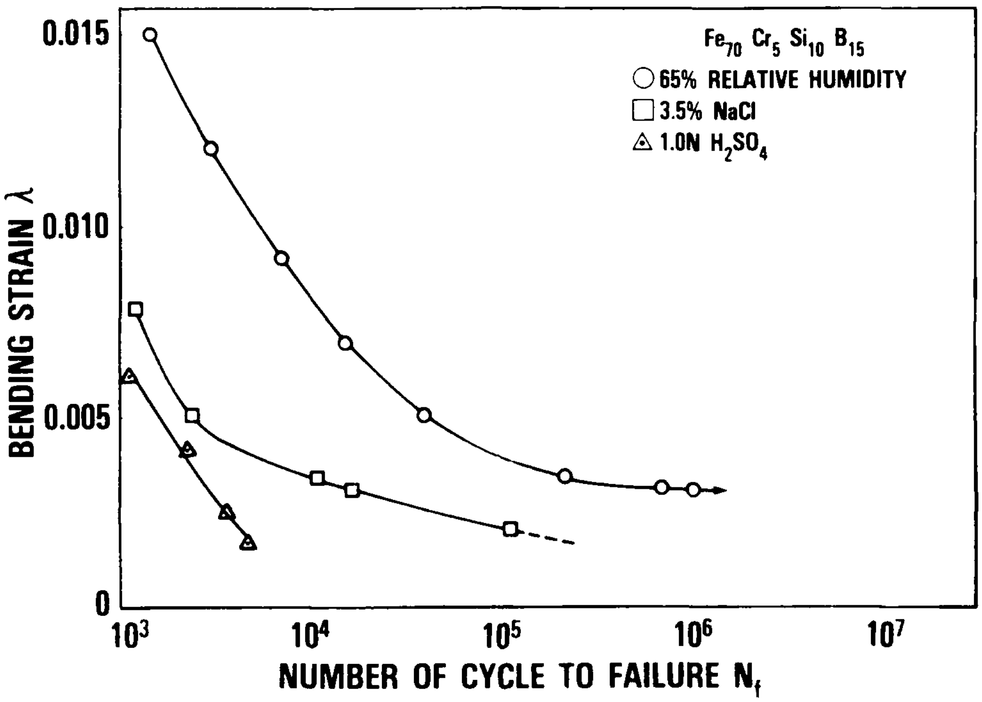

FIGURE 7. NUMBER OF CYCLES TO FAILURE AS A FUNCTION OF BENDING STRAIN FOR THE COMPOSITION $Fe_{70}Cr_5B_{15}Si_{10}$

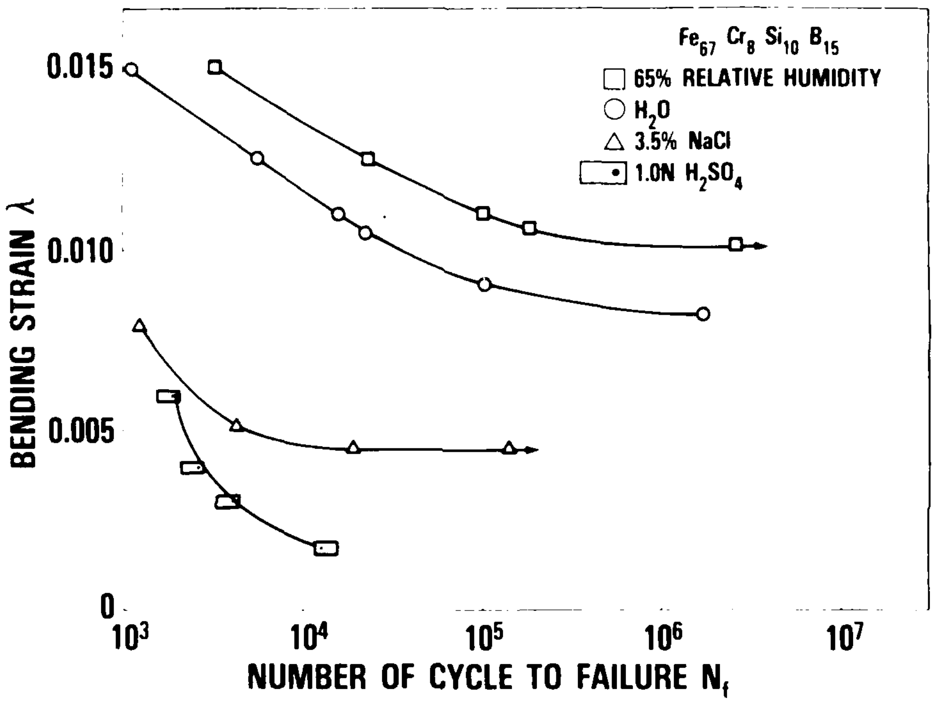

FIGURE 8. NUMBER OF CYCLES TO FAILURE AS A FUNCTION OF BENDING STRAIN FOR THE COMPOSITION $Fe_{67}Cr_8B_{15}Si_{10}$

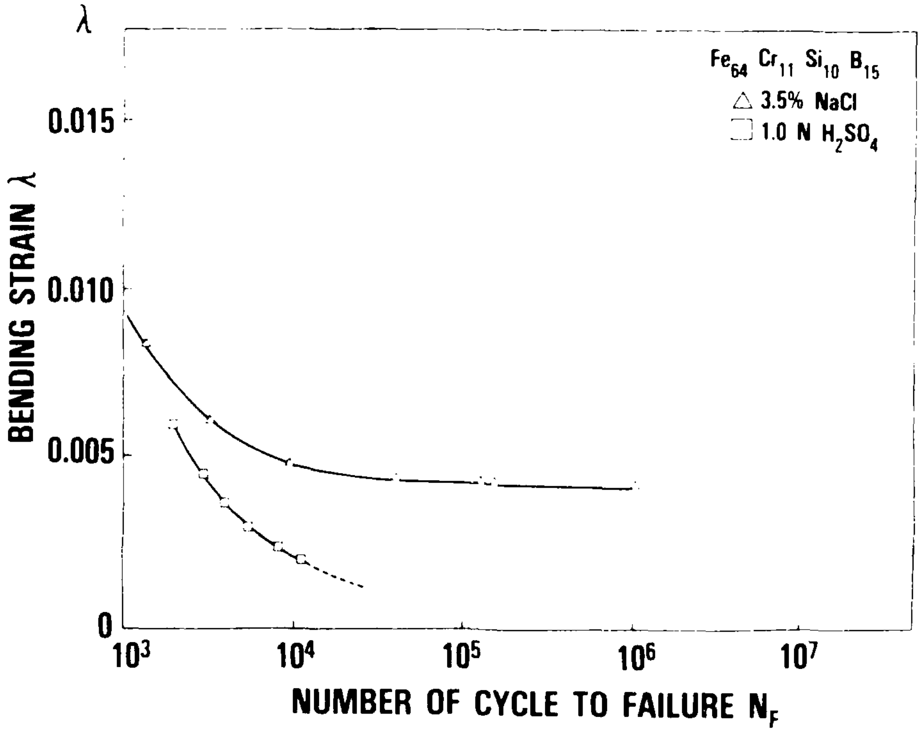

FIGURE 9. NUMBER OF CYCLES TO FAILURE AS A FUNCTION OF BENDING STRAIN FOR THE COMPOSITION $Fe_{64}Cr_{11}B_{15}Si_{10}$

cyclical strain was applied without interruption until failure. The time to failure in both cases was approximately the same as would be obtained for a "virgin" specimen. Since the control specimens remained in the solution, there was no removal of hydrogen. Thus, the bulk accumulation of hydrogen could not have been the cause of the fatigue failure in this case.

Extensive work has been done by Hashimoto et al.[6,7,8] on the mechanical failure of metallic glass ribbons in an acidic chloride environment. This work included tensile testing in a corrosive environment (with interruptions and baking similar to NSWC's tests discussed in previous paragraphs) and examination of the fracture surfaces. The evidence for brittle failure in an acidic environment due to bulk accumulation of hydrogen is convincing. However, it is interesting to note that fracture surfaces produced by failure in a neutral chloride environment differ from those produced in an acidified environment. It should also be noted that fatigue limits were observed only in cases of spontaneous passivation. In the case of an acidic environment or low chromium content in a neutral chloride environment, the general corrosion rate is relatively high, with hydrogen formed uniformly over the surface. In the case of spontaneous passivation, corrosion occurs primarily in cracks created in the passive film by the application of strain. Thus, it is reasonable to assume that the failure mechanism in the two cases will be substantially different.

A reasonable hypothesis for fatigue failure in the case of the spontaneously passivating specimens is that cracks in the passive film admit solution to the bare metal surface resulting in very rapid dissolution and formation of a "crevice." This bare surface repassivates very quickly, with the new passive film thickening over a period of time. If strain is again applied while the passive film in the crevice is still thin, a new crack will form in the crevice and repeated application of strain will result in the growth of this crevice. Failure occurs when a critical size is reached. Since the pH in the crevice can be much lower than in the bulk solution,[9] it is possible that some local accumulation of hydrogen occurs. If the cyclical application of strain is interrupted, the new passive film in the crevice thickens until it is no longer the weakest point, and next application of strain does not necessarily form a crack in the passive film at that site. If local hydrogen accumulation is a contributing factor to failure, the interruption in application of strain allows diffusion of hydrogen away from the site. More data is needed to determine the validity of this hypothesis, including measurement of the kinetics of passive film formation, rates of hydrogen diffusion in these metallic glasses, and a closer examination of the effects of composition and pH on the fatigue properties and passive film formation. Experiments to obtain this information are in progress.

Finally, an approximate measurement was made of the tensile strength of the wires by hanging weights on the ends of the wires. Tensile strengths (approximately 500 KSI) varied slightly with chromium content. More accurate measurement with an Instron tensile tester will be made in early FY87. The very high tensile strengths observed for wires indicate that the data previously reported for metallic glass ribbons is severely affected by the poor surface quality of the ribbon test samples. Ductile, corrosion resistant wires with yield strengths of 600 to 700 KSI are clearly possible.

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